Developing an anisotropic etch process for v-grove formation in GaAs

Nathaniel G. McKay[1]
University of Michigan College of Engineering, Ann Arbor, MI, 48109

The quantum dot nipi device is a promising approach to create ultra-high efficiency solar cells. One step required for the development of this device is an anisotropic etch process for v-grove formation. Anisotropic wet etching of GaAs was demonstrated using processes developed at Glenn Research Center. Photolithography was used to deposit a pattern of photoresist on a GaAs substrate. Samples of this substrate were then etched using a 2:1:50 solution of NH_4OH:H_2O_2:H_20. Samples were placed in the etchant solution for different periods of time to experimentally determine an etch rate of 613 $^{nm}/_{min}$. Anisotropism was confirmed through imaging of the etched features. The processing chemicals and equipment available at the facility were evaluated for future work developing the quantum dot nipi device.

Nomenclature

GaAs	=	Chemical formula for gallium arsenic
H_2O	=	Chemical formula for water
H_2O_2	=	Chemical formula for hydrogen peroxide
micron	=	micrometer ($1x10^{-6}$ meters)
min	=	minute (60 seconds)
NH_4OH	=	Chemical formula for ammonium hydroxide
nm	=	nanometer ($1x10^{-9}$ of meter)
RPM	=	rotations per minute
s	=	second (SI unit of time)
SEM	=	Scanning Electron Microscope
Si_3N_4	=	Chemical formula for silicon nitride
Å	=	Angstrom ($1x10^{-10}$ meters)

I. Introduction

Ultra-high efficiency solar cells have been a focus of photovoltaic research for some time. Conventional solar cell technology is ultimately limited by how efficient the new cells can get. The most recently developed cells are around 30% efficient. Increasing their efficiency involves adding more photovoltaic junctions and optimizing the device. Each additional junction gives a diminishing improvement on efficiency. Predictions say that a 50% efficient solar cell would require a 17 junction device (Ref. 1). Fabricating a device with this many junctions would be difficult and costly.

A novel device called a quantum dot nipi has been proposed which promises to achieve these high efficiency goals in a more practical manner. The quantum dot nipi device makes use of both its structure and material properties to achieve ultra-high efficiency. The structure of the quantum dot nipi is depicted in Fig. 1 on the next page. Multiple photovoltaic junctions are used to capture the majority light spectrum. These junctions are made from repeated horizontal negative doped (n) / undoped (i) / positive doped (p) GaAs layers. This repeating pattern is where the device gets the ‘nipi’ part of its name from. The structure is optimized to convert as much light to electricity as possible. Excess light transmitted through the junctions is sent back through the cell for a second pass by a reflective back coating, increasing the amount of optical absorption. Quantum dots embedded in the layers improve the electrical properties of the cell by increasing the current carrying capability. Vertical v-shaped ohmic

---

[1] Research Associate, RES0, Glenn Research Center, University of Michigan.

contacts are used, as opposed to the conventional horizontal contacts on the top and bottom of the cell. Using vertical contacts, the carriers conduct laterally in the horizontal layers instead of diffusing vertically through them. The quantum dot nipi cell is thus limited by carrier drift, not diffusion. This results in the device being more radiation resistant. The vertical contacts also connect the multiple junctions in parallel, leading to an output voltage characteristic of a single junction device. The quantum dot nipi device is projected to achieve efficiencies greater than 50%.

The focus on this project is to develop a formation process for the v-shaped groves that the vertical contacts will be grown in. This goal is part of the proposed research plan laid out by Wilt (Ref. 1). Metalorganic vapor phase epitaxy will eventually be used to grow the p and n-type ohmic contacts on the slanted walls of the v-groves. These slanted walls lie on the 111 plane of the substrate's crystal structure. For the deposition process a Si_3N_4 hardmask is needed. A conventional photoresist mask would melt away under the high tempters of the deposition process.

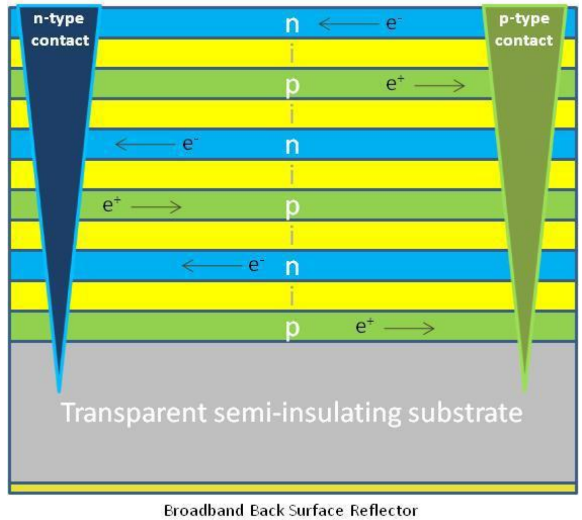


Figure 1. Quantum dot nipi device structure. *Carriers conduct laterally to v-shaped contacts. Creating a process to form the contact groves in a GaAs substrate is the focus of this project.*

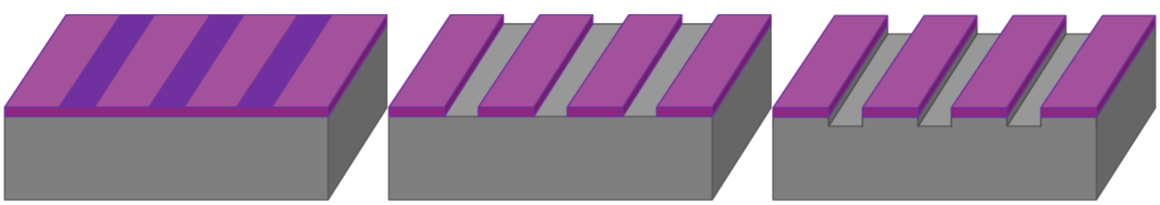
II. Background

Two important microfabrication processes are needed to etch the v-groves in the GaAs substrate. These processes are photolithography and wet etching. One goal of this project is to practice and develop these processes at Glenn Research Center.

A. Photolithography

Photolithography is the process by which a material called photoresist is patterned on a substrate. Photoresist is a special chemical which changes solubility properties once being exposed to ultraviolet light. By patterning the sample, you leave parts of the substrate exposed while others are covered with the photoresist. Then, using this pattern of photoresist, the substrate can be modified in select places. Common modifications are etching groves or depositing material.

The first step in patterning a sample is to deposit a thin uniform layer of photoresist onto the substrate wafer. A device spins the wafer while drops of viscous photoresist are placed on it. By knowing the properties of the photoresist and varying the RPM and spin time a desired thickness can be achieved. The sample is then 'soft' baked at a high tempter to drive off excess photoresist solvent. The resist covered wafer is placed on an auto exposure machine and brought into contact with a mask. A mask is a plane of glass with metal deposited in a pattern on one side. When ultraviolet light is shined on the sample, the mask shadows parts of the photoresist. The wafer is exposed for a period of time and then 'hard' baked to strengthen the photoresist coating. Depending on the type of photoresist, the sample may be given a flood exposure of ultraviolet light afterwards. Once ready for development, the sample is placed into a developer solution that dissolves away the soluble areas of the photoresist. For positive photoresist, the areas exposed to light dissolve away. For negative photoresist the parts cast in shadow dissolve away. Three important steps of this microfabrication process are depicted in Fig. 2.



(a) **(b)** **(c)**

Figure 2. Progression of photolithography process. *a) Mask is removed showing areas of photoresist shadowed from UV light in dark purple. b) Negative type photoresist becomes soluble where not exposed to light and dissolves away in developer solution. c) Exposed substrate is later etched in desired pattern.*

B. Anisotropic Wet Etching

Wet etching is the process of dissolving away, or etching, the upper most layers of an exposed crystal substrate by submerging the sample in a chemical solution called an etchant. The etchant solution is created to etch a specific substrate in a desired way. Different etchants have different etch rates and different etching characteristics. The etch rate is the rate at which the depth of the etch increases with time. Knowing the etch rate you can control how deeply features are etched into the substrate. Different etch characteristics, such as shape of the etched grove, can also be controlled. Anisotropic wet etching produces trapezoid shaped groves. This is due to the crystal structure of the substrate. The bottom horizontal surface lies along the <100> crystal plane and the inward slanted walls lie along the <111> crystal plane. The slanted walls are at a 54.7 degree angle with respect the horizontal. Undercutting of the mask, in which the substrate etches under the photoresist, is another characteristic of the anisotropic etch process. Figure 3 depicts the anisotropic etch characteristics. Under the right circumstances an anisotropic etch will reach a depth where the slanted walls intersect each other and form a ‘v’ shape. This ‘v’ shape is desirable for use in the quantum dot nipi device.

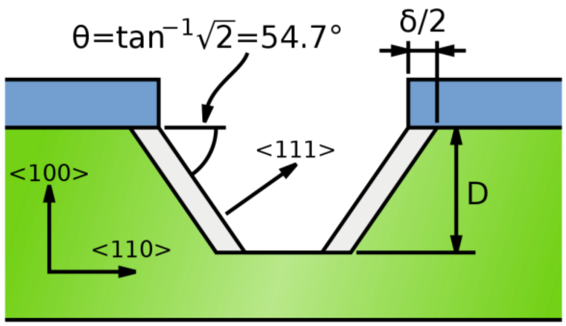


Figure 3. Anisotropic Etch Characteristics. *The trapezoid shape results from etching slanted walls along the <111> crystal plane of the substrate. Light grey represents the part of etch that undercuts mask.*

III. Procedure

Specific procedures for the photolithography and etching process are detailed in this section. Also detailed are the methods used to experimentally determine the etch rate and verify an anisotropic etch. Six samples were eventually etched for different periods of time and analyzed. These samples are described in Table 1.

	Sample 1	*Sample 2*	*Sample 3*	*Sample 4*	*Sample 5*	*Sample 6*
Photolithography process	**1**	**2**	**3**	**3**	**3**	**3**
Time between photolith. and etch	**2 weeks**	**1 hour**	**24 hours**	**24 hours**	**24 hours**	**24 hours**
Etch time	**2 min**	**4 min**	**1 min**	**2 min**	**3 min**	**4 min**

Table 1. Description of the 6 Samples. *The photolithography process, etch time, and the wait between photoresist development and etching describes the six samples.*

A. Photolithography Process

After first practicing on silicon wafers, three photolithography processes were preformed to create the six samples. Negative type AZ 5218E photoresist was spun on the GaAs samples at 3000 RPM for 55 seconds. Measurements with the profiler taken after development determined the PR thickness to be approximately 2.7 microns. After spinning, the resist layer was inspected for defects such as large distortions from dust on the sample. If large distortions were present the resist was removed from the wafer using acetone and the spin deposition process was repeated. After photoresist deposition the samples were soft baked on a hotplate at 98°C for 4 min. The samples were then place on the platform of the auto exposure machine and brought into contact with a mask. The mask used for all samples was chosen due to its diversity in feature size and orientation. The masked samples then underwent a 5 second exposure to UV light. Samples were removed and hard baked a 119°C for 4 min. Following the hard bake the samples underwent a 55 second UV flood exposure. A 1:5 solution of AZ351:H_2O was used to develop the photoresist. Approximate time of development was 50 seconds. The samples were gently agitated while submerged in the developer.

Samples 1 and 2 each underwent and independent photolithography process. This is because the GaAs wafer they are made from broke into large shards before the photolithography process could begin on the whole wafer. Samples 3 through 6 were processed on the same wafer in a third photolithography process. The wafer was later broken into quadrants before etching, as shown in Image 1 on the next page.

B. Anisotropic Etching Process

The GaAs samples were etched using a 2:1:50 solution of NH_4OH:H_2O_2:H_2O. Sample 1 was left for 2 weeks before being developed and etched. This is because new developer needed to be ordered and shipped. Sample 2 was etched on the same day within hours after development. Samples 3 through 6 were etched approximately 24 hours after development. Samples were submerged in the etchant and gently agitated for varying periods of time. Samples 1 and 4 were etched for 2 min. Samples 2 and 6 were etched for 4 min. Samples 3 and 5 were etched for 1 min and 3 min, respectively. After the etching period the samples were submerged in a beaker of deionized water and thoroughly rinsed under a deionized water tap.

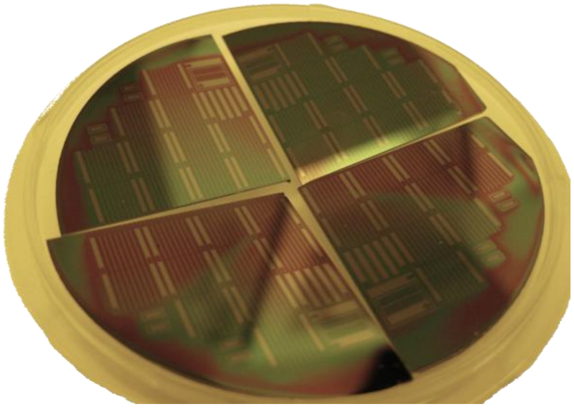


Image 1. Processed wafer split into quadrants. *Samples 3 through 6 made from same GaAs wafer.*

C. Determining Etch Rate

The etch rate was determined by comparing the measured valley depth of the six samples to the time period they were submerged in the etchant. Once etched, each sample was broken in two pieces. One half was stripped of photoresist with an acetone rinse. Photoresist was removed to make measuring the etch depth with the profiler straightforward. The other half of the sample with the photoresist still on it was preserved for SEM imaging. A profiler was used to measure the relative heights of the samples features. A profiler measured depth by moving a very fine needle across a surface and recording the vertical displacement of the needle tip. Profiler scans were taken across four distinct features present in every sample. Four measurements were taken in the interest of reducing random error. Very narrow groves gave inaccurate measurements of depth as the needle tip was too wide to fit all the way down into the grove.

D. Verification of Etch Anisotropy

To verify that the etch was anisotropic, the sample was imaged with a scanning electron microscope (SEM). Images were taken of similar features among the stripped halves of samples 3, 4, 5 and 6 to determine how the etch progressed over time. Images of photoresist undercutting were also taken among the preserved haves of samples 3 and 6. Finally the stripped halves of samples 3 and 6 were broken along feature pattern lines to achieve edge on views of the narrow groves. By comparing the angle of the slanted etched wall from the SEM image to the expected 54.7 degree angle, anisotropy was confirmed.

IV. Results

Results from the profiler measurements are plotted in Fig 4. Four depth measurements from each of the 6 samples are plotted on this graph. The samples vary in the amount of time they were etched for. The etch depth, in Å, is compared to the etch time, in sec. A linear fit to the data gives an etch rate of 102 Å / s. This converts to 613 nm / min (the conventional etch rate units). Outlier points, circled in the figure, are the result of the profiler probe tip being too wide to fit all the way down into the narrow gaps. These outliers were all measurements of the same extremely narrow feature, and are excluded from the linear fit.

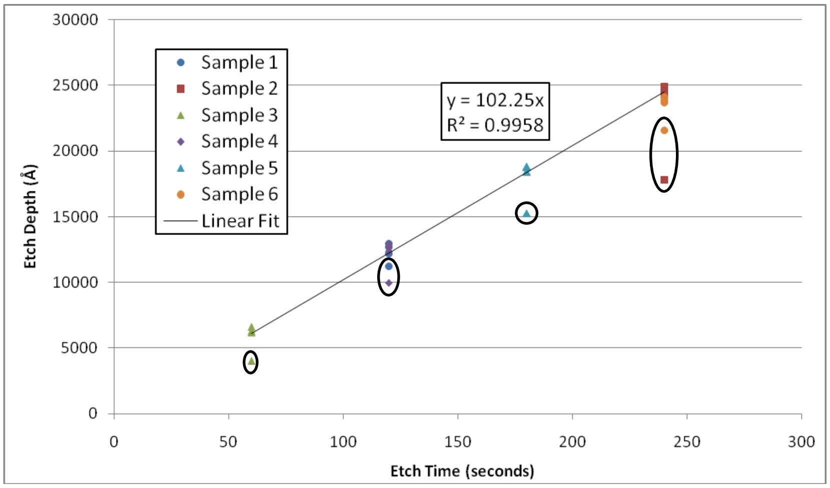
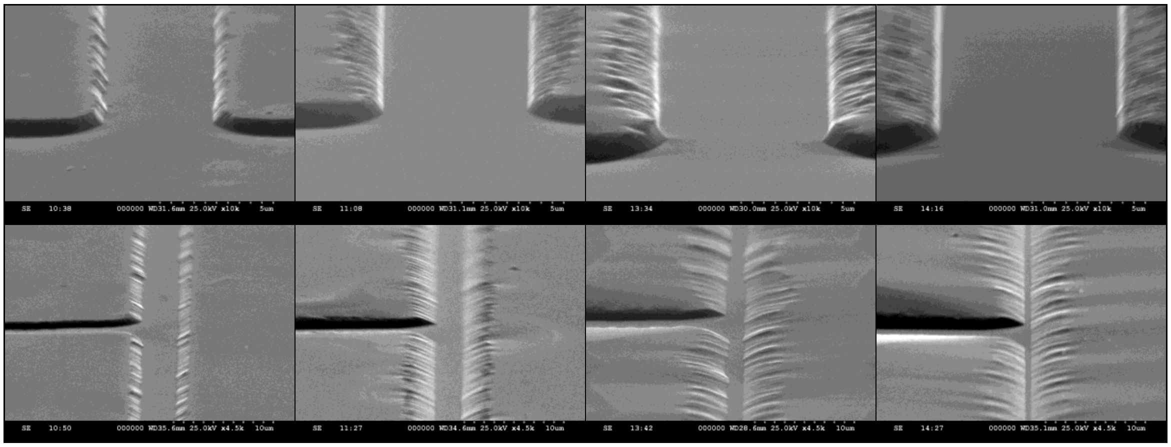


Figure 4. Etch depth as a function of etch time. *Linear fit to the profiler data gives etch rate of 102 Å / min. Circled data points excluded from fit.*



(a) (b) (c) (d)

Image 2. Progression of etch over time. *All samples imaged at 80 degrees. a) Views of sample 3, etched for 1 min. b) Views of sample 4, etched for 2 min. c) Views of sample 5, etched for 3 min. d) Views of sample 6 etched for 4 min.*

SEM images of two different feature sizes on each of samples 3 through 6 are shown in Img. 2. As time progresses it is clear that the etched valleys grow deeper. The bottom set of images depict a v-shaped feature forming as the grove deepens, bringing the slanted walls together. The top set of images shows a valley that grows both deeper and wider. The top and bottom features are oriented 90 degrees with respect to each other. The widening characteristic apparent in the top set of images may owe itself to the difference in crystal structure, as the groves are in fact etched along a different set of planes. The jagged groves and curved edges are the result of undercutting and pealing of the photoresist mask. Image 3 shows undercutting and severe pealing of the photoresist. Undercutting of the mask is characteristic of an anisotropic etch. Pealing of the mask it due to poor resist adhesion to the substrate.

Anisotropy is proved using images of the etched features. Image 4 shows an edge on view of an etched gap from sample 6. An enlarged view of the gap's slanted wall is also shown. Drawn on this enlarged view is a horizontal line that matches with the flat bottom of the etched groove. Another line is drawn at 54.7 degrees with respect to this horizontal. The slanted wall is found to match up perfectly with the angled line, proving the etch is anisotropic.

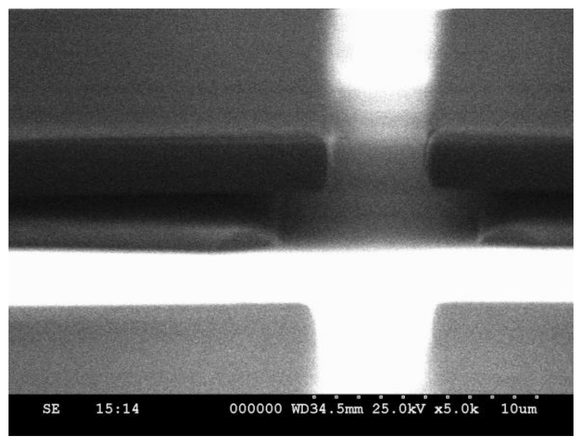
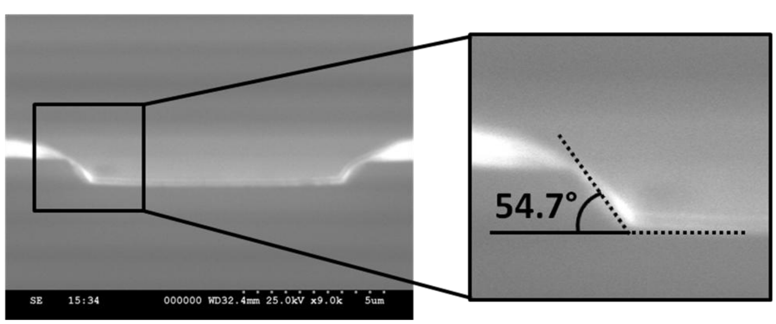


Image 3. Undercutting of Photoresist. *Preserved half of sample 6 shows sever undercutting and pealing of photoresist. Viewed at 88 degrees.*



(a) (b)

Image 4. Confirmation of Anisotropic Etch. *a) Edge on view of narrow valley. b) Anisotropic etch conformed by zoomed view of slanted edge showing 54.7 degree angle.*

V. Conclusion

The goal of this project was to develop an anisotropic etch process for v-grove formation. Through profiler measurements and SEM imaging of the six etched samples, an etch rate was experimentally determined and the etch was confirmed to be anisotropic. The etching process preformed at Glenn Research Center has now been documented with these characteristics. Future work on this project should focus on eliminating etching defects, such as the jagged groves and pealing of the photoresist mask. Focus should be given to the creation of a silicon nitride hard mask for etching these features. Eventually this hard mask will play an important role in the deposition of the p and n-type contacts. The way in which a grove is etched layers of doped GaAs should also be investigated.

Acknowledgments

I would like to thank Sheila G. Bailey, my mentor, and David v. Forbes for their support and guidance with my project. I would like to thank David Wolford for teaching me the photolithography process. I would also like to thank Bobby for teaching me how to use the scanning electron microscope.

References

[1] Wilt, David, "A Pathway to Ultra-High Efficiency Photovoltaics," Air Force Research Laboratory, KAFB, 2009